

Anomalous correlation effects and unique phase diagram of electron doped FeSe revealed by angle resolved photoemission spectroscopy

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In FeSe-derived superconductors, the lack of a systematic and clean control on the carrier concentration prevents the comprehensive understanding on the phase diagram and the interplay between different phases. Here by K dosing and angle resolved photoemission study on thick FeSe films and FeSe_{0.93}S_{0.07} bulk crystals, the phase diagram of FeSe as a function of electron doping is established, which is extraordinarily different from other Fe-based superconductors. The correlation strength remarkably increases with increasing doping, while an insulating phase emerges in the heavily overdoped regime. Between the nematic phase and the insulating phase, a dome of enhanced superconductivity is observed, with the maximum superconducting transition temperature of 44±2 K. The enhanced superconductivity is independent of the thickness of FeSe, indicating that it is intrinsic to FeSe. Our findings provide an ideal system with variable doping for understanding the different phases and rich physics in the FeSe family.

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The physical properties of correlated materials are sensitive to various parameters like carrier doping. Fine tuning on the carrier doping allows investigating the rich phase diagrams and helps understanding the interplay and mechanism of different phases. However, for FeSe, a prototypical system of Fe-based superconductors with the simplest structure, the systematic doping control is still lacking. Although heavily electron doping has been achieved in intercalated FeSe crystals like A_xFe_{2-y}Se₂ (A=K, Rb, Cs, Tl/K) [1, 2] and (Li_{0.8}Fe_{0.2})OHFeSe [3], the doping levels are discrete and fixed. Moreover, the phase separation in A_xFe_{2-y}Se₂ [4–8] complicates the studies on the intrinsic superconductivity. In (Li_{0.8}Fe_{0.2})OHFeSe, the polar surface prevents the observation of intrinsic bulk electronic structure in surface sensitive angle resolved photoemission spectroscopy (ARPES) measurements [9]. Single-layer FeSe films on SrTiO₃ or BaTiO₃ [10–15] are another type of heavily electron doped FeSe-based superconductors, whose superconducting transition temperature (T_c) could be above 65 K [15–17]. However, besides the electron doping, the interfacial effects are suggested as a crucial factor for the enhanced superconductivity [15, 18]. The lack of a clean FeSe system with systematic doping control prevents a full investigation on the phase diagram, and hampers the comprehensive understanding of the relationship between superconductivity and other ordered phases.

Recently, post-annealing in vacuum has been reported to effectively tune the doping in single-layer FeSe films on SrTiO₃ substrate, however, this approach fails in inducing superconductivity in the second layer FeSe [13, 19]. Alternatively, by doping control with K dosing, a superconducting dome has been observed in FeSe films of 3 uc (unit cell) thickness [20].

However, no superconductivity was found in 20 uc FeSe films at 13 K at any doping [20], therefore the enhanced superconductivity in 3uc FeSe/SrTiO₃ was attributed to some interface effect.

In this paper, we report the observation of an enhanced superconductivity in both thick FeSe films up to 50 uc and FeSe_{0.93}S_{0.07} bulk crystals upon K dosing. The size of the superconducting gap and the T_c are identical on FeSe films with different thicknesses and on FeSe_{0.93}S_{0.07} bulk crystals, indicating that the superconductivity is intrinsic to FeSe without any interfacial effects. More importantly, from the doping evolution of electronic structure and the superconducting behavior, a rich phase diagram of FeSe has been established, which show unique characteristics distinct from other Fe-based superconductors. We observe an anomalous enhancement of correlation strength with increasing doping. The dome of enhanced superconductivity with the highest T_c ~44±2 K is sandwiched between a nematic phase and a correlation induced insulating phase. These results provide a global picture of the interplay among nematic order, superconductivity, and electron correlations in the FeSe family.

The thick FeSe films were grown on TiO₂ terminated Nb:SrTiO₃ (001) substrates following the method described in our previous reports [12]. The electron doping is induced by depositing K atoms with a commercial SAES alkali dispenser. The doping levels no more than 0.158 were determined by ARPES based on Luttinger volume of Fermi surfaces, while the others were estimated according to the amount of K deposited. The single crystal of FeSe_{0.93}S_{0.07} (T_c=9.5 K) were grown using the flux method [21, 22]. ARPES data were taken under ultrahigh vacuum of 1.5×10⁻¹¹ mbar, with a discharge

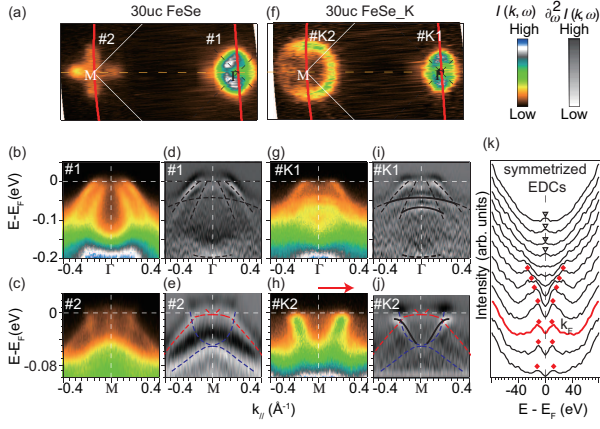


FIG. 1: (color online). (a) The photoemission intensity mapping at the Fermi energy (E_F) from a 30 uc FeSe film. (b), (d) The photoemission intensity along cut #1 in (a) and the corresponding second derivative, respectively. (c), (e) The same as (b) and (d) but along cut #2 in (a). (f) The photoemission intensity mapping at E_F from a 30 uc FeSe film with electron doping $x=0.09$ after K dosing. (g), (i) The photoemission intensity along cut #K1 in (a) and the corresponding second derivative, respectively. (h), (j) The same as (g) and (i) but along cut #K2 in (a). (k) The symmetrized energy distribution curves (EDCs) along the momenta indicated by the arrows in panel (h). The data in (h), (j), and (k) were taken at 31 K, the others at 70 K.

lamp (21.2 eV He-I α light) and a Scienta R4000 electron analyzer. The energy resolution is 7 meV and angular resolution is 0.3°. The sample growth/cleaving, K deposition, and ARPES measurement were all conducted in-situ.

Figure 1 shows the band structures of a 30 unit cell (uc) thick FeSe before and after K dosing. Before K dosing, the band structures of the 30 uc FeSe film is consistent with those in the previous reports on thick FeSe films [12, 23] and bulk FeSe crystals [24–27]. As shown in Figs. 1(a), the Fermi surface consists of hole pockets at Γ and dumb bell shaped spectral weight at M. There are two hole-like bands crossing E_F around Γ (Fig. 1(b) and 1(d)). Around M, the complex band structure is caused by the splitting of bands with d_{xz} and d_{yz} orbital characters (Figs. 1(c) and 1(e)) [12, 23], which reflects the orbital ordering or nematicity. After K-dosing, a circular pocket appears around M [Figs. 1(f)]. The photoemission spectra show the superposition of two sets of band structures. One set of bands follow the band structure of undoped FeSe and show weaker spectral weight, as indicated by dashed curves in Figs. 1(i) and 1(j). Considering the finite detection depth of our ARPES measurement [12], these bands are attributed to the FeSe beneath the topmost layer. We found that the K atoms mainly dope the topmost unit cell, while the layers beneath remain undoped. The second set of bands with the prominent photoemission spectral weight come from the topmost layer and are heavily electron doped. Around Γ , the two hole-like bands shift to higher binding energies and become flatter (Figs. 1(g) and 1(i)). A simple electron-like band appears around M (Fig. 1(h) and 1(j)), in-

dicating that the nematic order is suppressed [12]. The carrier concentration is 9% per Fe ($x=0.09$) according to the Fermi surface volume. Intriguingly, the symmetrized energy distribution curves (EDCs) in Fig. 1(k) exhibit back bending after passing the Fermi momentum (k_F) without crossing the Fermi energy. The sharp coherence peaks and back-bending behavior are hallmarks of Bogoliubov quasiparticle, which implies superconductivity in the K-dosed FeSe. The superconducting gap size is about 10 meV at 31 K, suggesting that the T_c in FeSe is significantly enhanced from the bulk T_c of 8 K. The weak features from the undoped inner layers remain gapless around M [Fig. 1(k)], indicating that the superconductivity only exists in the doped topmost layer, without proximity into the layers beneath. Our results are in contrast to the absence of superconductivity in 30 uc Fe_{0.92}Co_{0.08}Se thick films [15], where the superconductivity is probably killed by the strong scattering of the in-FeSe-plane Co ions [28]. The enhanced superconductivity here suggest that the off-FeSe-plane K introduces much weaker impurity scatterings [29].

Figure 2 shows the thickness dependence of superconducting gap. At electron doping level around $x=0.09$, back-bending dispersions and superconducting gaps are observed for all the K-dosed FeSe films with thicknesses varying from 4 uc to 50 uc [Figs. 2(a)–2(e)]. Moreover, for K-dosed FeSe_{0.93}S_{0.07} bulk crystals with no FeSe/oxide interface, superconducting gap is also observed [Figs. 2(f)]. At 31 K, the gap size Δ is about 10 meV for all the films and bulk FeSe_{0.93}S_{0.07} [Fig. 2(g)]. For example, as shown in Fig. 2(h), the gap size of 30 uc film is identical to that of 10 uc film at 42 K. With increasing temperature, the superconducting gap closes around 44 ± 2 K for both films with thickness of 10 uc [Fig. 2(i)] and 30 uc [Fig. 2(j)]. Their temperature dependences are summarized in Fig. 2(k), which can be well fit by the same Bardeen-Cooper-Schrieffer formula (BCS formula). Therefore, for thick films or bulk material, the enhanced superconductivity here is intrinsic to electron doped FeSe, and does not dependent on the thickness or the FeSe/SrTiO₃ interface, which is distinct from the previous report on K-dosed FeSe [20].

The evolution of the electronic structure with electron doping is further studied by systematically altering the K dosing. Figure 3(a) shows the spectra around Γ as a function of doping. For all the spectra with different doping levels, dispersions from the undoped FeSe layers underneath are always visible, which is independent of the doping of the surface. When the electron doping level x of the surface FeSe layer is increased from 0.033 to 0.127, two hole-like bands gradually shift to higher binding energy [Figs. 3(a) and 3(d)]. Simultaneously, these two bands become flat with x from 0.087 to 0.127 [Figure 3(a)], then become incoherent for $x > 0.137$, and disappears for $x \sim 0.189$, indicating increasing correlation strength. From the EDCs at Γ [Figure 3(d)], we can see that the two quasiparticle peaks turn into incoherent spectral weight (pink shadow) when $x=0.137$ and 0.158, and totally diminish when x reaches 0.189. After it is further doped to $x \sim 0.228$, a small electron-like band emerges around the zone

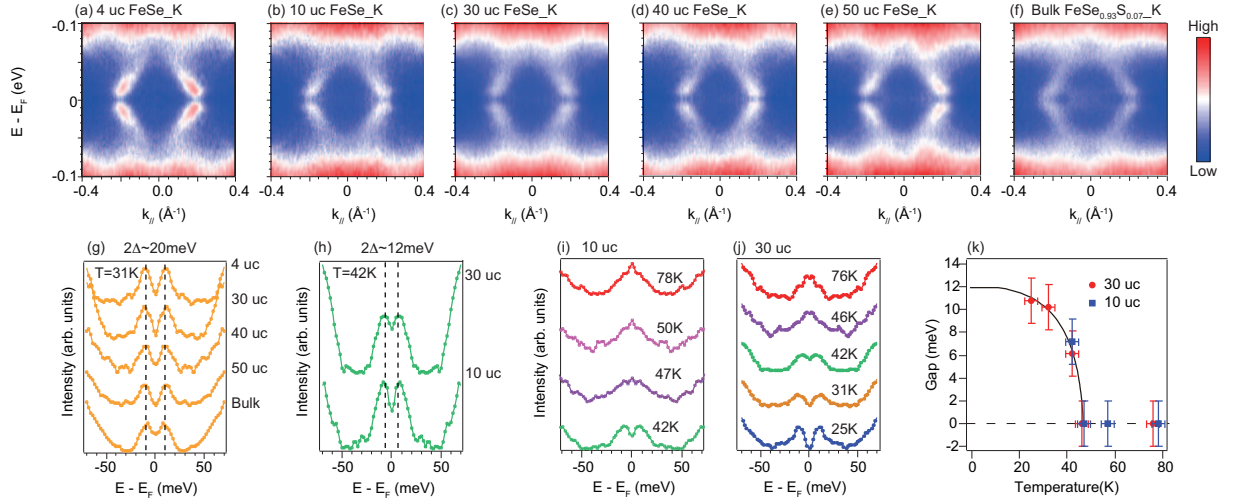


FIG. 2: (color online). (a)-(f) The symmetrized spectra of K-dosed FeSe films with thickness of 4 uc, 10 uc, 30 uc, 40 uc, 50 uc, and K-dosed bulk FeSe_{0.93}S_{0.07}, respectively. The data of 10 uc were taken at 42 K, the others at 31 K. (g) The symmetrized EDCs at k_F for the FeSe films with different thicknesses and FeSe_{0.93}S_{0.07} bulk crystal at 31 K after K dosing. (h) The symmetrized EDCs at k_F for thicknesses of 10 uc and 30 uc at 42 K after K dosing. (i), (j) Temperature dependences of the symmetrized EDCs at k_F for thicknesses of 10 uc and 30 uc, respectively. (k) The superconducting gap size as a function of temperature from the data in panels (i) and (j). The solid curve is the fitted result of BCS formula. The doping level is around 0.09.

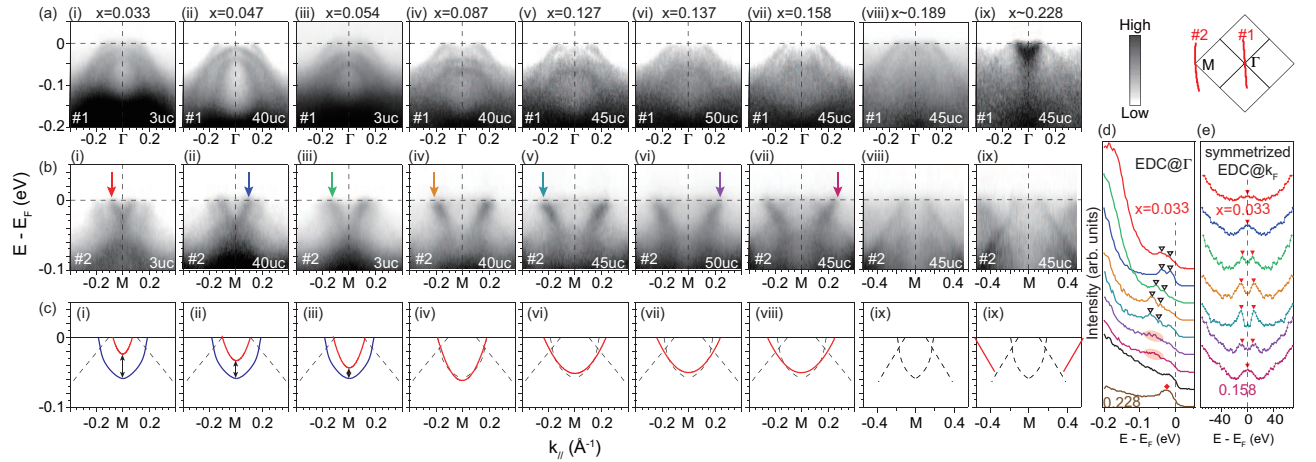


FIG. 3: (color online). (a) The evolution of photoemission spectra along cut #1 as a function of increasing electron doping. (b) The doping dependent evolution of photoemission spectra along cut #2. The upper-right inset shows the locations of cuts #1 and #2. (c) The doping dependent evolution of the dispersions extracted from (b). The solid curves indicate the electron-like bands of the doped surface layer, while the dashed curves indicate the dispersions from inner layers without doping. (d) The EDCs at Γ with different dopings. (e) The symmetrized EDCs showing the evolution of superconducting gap as a function of doping. The momenta of spectra were indicated by the arrows in panels (b) with corresponding colors. The data in this figure were taken at 31 K, except those for $x=0.054$, which were taken at 25 K.

center [Figure 3(a)], and a well defined quasiparticle peak appears again [Figure 3(d)].

Around M, two electron-like bands are observed for the K-dosed FeSe with $x=0.033$ [Fig. 3(b)], which are illustrated by the solid curves in Fig. 3(c). Compared with the undoped band structure in Figs. 1(e), the upper band shifts downwards and the lower band remains at a fixed binding energy. Since the energy separation between them reflects the strength of the nematic order [23], the decreased energy separation with increasing doping indicates the weakening of nematicity. Even-

tually, these two bands become degenerate at $x = 0.087$, indicating the complete suppression of nematicity. As the doping further increases, the electron band gradually becomes flatter, indicating the enhanced correlation, consistent with the behaviors of the bands around Γ . Remarkably, when $x \sim 0.189$, the spectral weight from the topmost layer depletes, while only the spectra from the inner layer remains around the zone corner. The absence of spectral weight for the K-dosed bands both around Γ and M near E_F indicates that FeSe turns into an insulating state with $x \sim 0.189$. As the doping further in-

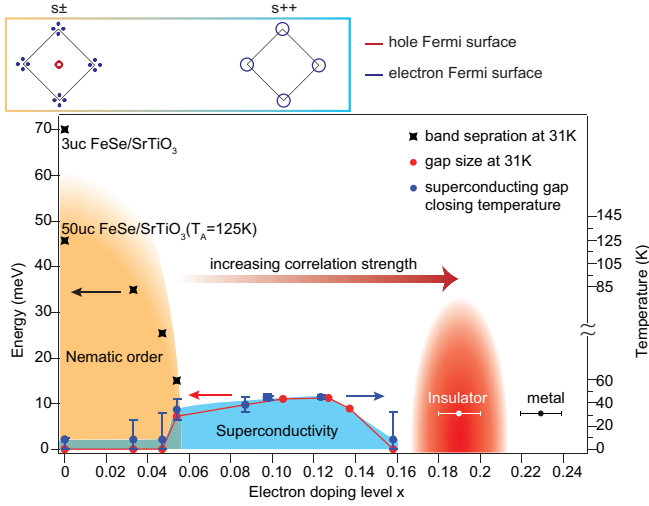


FIG. 4: (color online). Phase diagram of electron doped FeSe, and the summarize of the nematic band splitting, superconducting gap size, and the T_c as a function of doping. The nematic band splitting were determined by the energy difference between band bottoms in Fig. 3(c)(i-iv), while the undoped value is from ref. 12. For doping values without generating superconducting gap at 31 K, T_c 's were set as the T_c of bulk FeSe, 8 K. The other data points of T_c were determined by the superconducting gap-closing temperature. The gap size at 31 K were obtained by fitting the symmetrized spectra at k_F . The upper inset illustrates the different Fermi surface topology and superconducting pairing symmetry of undoped FeSe and heavily electron doped FeSe.

creases to about 0.228, the topmost layer reenters a metallic state with a very large electron pocket. The data shown here were taken on four different samples with the thickness of 3uc, 40uc, 45uc, 50uc [noted in Figs. 3(a) and 3(c)], respectively, and have been reproduced in another 6 samples. The band dispersions evolve in the same trend regardless of film thickness.

The symmetrized EDCs in Fig. 3(e) give the doping dependence of the superconducting gap. The gap opening is observed at the doping level 0.054, indicating a coexisting regime that the superconductivity is enhanced while the nematicity is not fully suppressed. The gap size increases to ~ 10 meV at $x=0.087$, and does not change significantly from $x=0.087$ to $x=0.127$, and then decreases to 7 meV at $x=0.137$. The gap closes for $x=0.158$, indicating that the T_c is below 31 K. The sample with high doping level around 0.228 is not superconducting at 31 K (see Supplementary Information).

Figure 4 summarizes the observed phases in K-doped FeSe, and establishes a doping dependence phase diagram of K-doped FeSe. By summarizing the superconducting gap size at 31 K, and the T_c determined by the gap-closing temperature (Supplementary Information), we have observed a superconducting dome with enhanced superconductivity near the nematic phase. The maximum T_c is 44 ± 2 K, which is lower than the gap-closing temperature of 65 K in single-layer FeSe/SrTiO₃. The 21 K higher T_c in single-layer FeSe/SrTiO₃ could be attributed to additional T_c enhancement due to certain interface effect beyond carrier doping.

The phase diagram of electron doped FeSe has some essential ingredients of a canonical phase diagrams of iron based superconductors. For example, the superconductivity is enhanced when the nematic order is suppressed, and the superconductivity diminishes at high electron doping. However from the electronic structure perspective, it is actually rather distinctive from others and exhibits the following unique features.

1. Both nematic order and superconductivity coexist in undoped FeSe crystal at low temperatures [24–27]. The coexistence doping ranges from 0 to about 0.054, within which T_c even reaches above 25 K.
2. After the full suppression of nematicity, the bandwidth narrows with increased electron doping, indicating enhanced correlation. This is in contrast to many iron based superconductors such as LiFe_{1-x}Co_xAs and NaFe_{1-x}Co_xAs, where the bandwidth increases rapidly with electron doping [29].
3. At the overdoped side with increasing electron doping, the system enters an insulating phase, which is quite extraordinary since most cuprates and iron-based superconductors become more Fermi-liquid-like and show decreasing correlation strength at the overdoped regime. This insulating phase is likely a Mott insulator driven by the increased correlations. A second antiferromagnetic phase has been reported before in heavily electron doped LaFeAsO_{1-x}H_x ($x \sim 0.5$) [30], and a superconductor-insulator transition has been reported in heavily electron doped (Li,Fe)OHFeSe through liquid gating [31]. The insulating phase discovered here is likely intimately related to those phases. In addition, an insulator to metal transition occurs with further electron doping in the far overdoped side.
4. The Fermi surface of FeSe consists of hole pockets at Γ and electron pockets around M [12, 24–27], where the superconducting pairing symmetry is most likely to be s_{\pm} type with sign reversal between the hole and electron pockets, as evidenced by previous experiments [32]. On the other hand, the Fermi surface of the electron doped FeSe consists of only electron pockets, where the pairing symmetry was found to be plain s-wave without any sign change for FeSe/STO [33] and (Li_{0.8}Fe_{0.2})OHFeSe [34].

To summarize, we obtained an enhanced superconductivity with T_c up to 44 ± 2 K in thick FeSe films and FeSe_{0.93}S_{0.07} bulk crystals by K-dosing. The superconductivity is independent on the film thickness and is intrinsic to K-doped FeSe without the contribution from interface. Furthermore, we have observed a systematic evolution of electronic structure and established a unique phase diagram of FeSe with electron doping. A new insulating phase is observed at high doping levels, which is likely induced by increased correlation strength. Our findings show that K-doped FeSe can serve as a new and clean

playground with well-controlled electron doping and weak impurity scatterings for further studying the relations between different phases, such as the evolution between different pairing symmetries, the superconductor-insulator transition, and the coexisting nematic order and superconductivity.

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